The effect of lubricating oil on diesel engine PCDD/F and PCB emissions

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Introduction

In 2004 a test programme was initiated to determine whether the chlorine content of lubricating oils had a measurable effect on emissions of PCDD/F and PCB from internal combustion engines. The project is part of a life-cycle assessment on the environmental impacts of lubricants designed to determine what the effect of a restriction on chlorine content in oil would have on the life-cycle impacts.

A review of the literature showed that no detailed study on the effects of chlorine in engine oil on emissions of dioxins had been carried out, although one or two tests had been included in other programmes using different oil formulations. Essers et al (1992)[1] carried out a series of tests on a number of engines in order to assess emissions of PCDD/F from petrol and diesel vehicles. Results from these tests appeared to show that emissions increased when using low chlorine oil.

Methodology

Since emissions of dioxins from vehicles tend to be extremely low, a test programme was designed that would provide a real-world condition but would maximise the possible effects and used measurement methods designed to ensure that any effects would be detected.

The very widely used VW 1.9 TDi engine was selected and the oils were formulated with standard components to give a realistic range of residual chlorine. No exhaust gas treatment was applied, the engine was run on a computer-controlled dynamometer under steady-state conditions to enable better repeatability. The conditions chosen also ensured reasonably high oil consumption. Stock reference fuel with a chlorine content of 0.71ppm was used, this was at the lower end of the range of diesel samples we analysed.

The engine was flushed three times between runs for each test to ensure that there was minimal cross-contamination of the lubricating oils from one test to the next.

The three oils were used for the tests were derived from a fully formulated lubricant meeting the performance of a 5W-30 ACEA A3/B3/B4/C3, MB229.31. with residual chlorine controlled by the dispersant choice in the range that might be expected in practice (12ppm, 131ppm, 259 ppm).

Sampling for the first block of tests was by the “filter-condenser” method based on the standard US EPA method 23 and in line with the European standard EN 1948. The apparatus consisted of a heated titanium probe inserted into the exhaust, a filter (Whatman GF-A) to remove particulate matter held in an oven at under 125ºC, a condenser, resin trap (XAD-2 resin), followed by moisture removal, pump and dry gas meter. Sample extraction and analysis for target congeners and homologue groups was according to EN 1948 by high-resolution gas chromatography and mass spectrometry. For further tests the train will be enhanced to increase the volume of gases and reduce detection limits. New, laboratory-cleaned probe, glassware and resin were used for each test.

Results

The test series was successful and data on dioxins was obtained from each run. The results from the first and second run are considered suspect due mainly to the unusual pattern of PCDD/F and PCB, possibly linked to residual contamination in the new engine.

In all tests emissions concentrations were low and in runs 6, 7 and 8 five to seven of the 17 target congeners were not detected, 2,3,7,8 TCDD was only detected in the first run.

Run Number	Oil chlorine level ppm	Measured dioxin concentration pg I-TEQ/Nm^3 @11% O_2	Dioxin emission expressed as pg I-TEQ/l of fuel consumed
1	259	8.94	164.5
2	259	3.28	60.3
3	12	1.61	29.7
4	12	1.87	34.5
5	131	2.52	46.4
6	131	0.66	12.1
7	259	0.33	6.0
8	12	0.18	3.3
9	259	2.30	42.3
10	12	1.54	28.3
11	131	2.67	49.0

Notes: non detected congeners set to zero

Table 1 Summary of Hazelwood results

Table 1 tabulates the results. Figure 1 plots emissions (expressed as pg I-TEQ/l of fuel consumed) for each run along with the input of chlorine to the system from air, fuel and oil (consumption measured for each test). The data cover a wide range with concentrations from 0.18 to 2.67 pg I-TEQ/Nm^3 dry gas at 11% O_2 (excluding the first two runs), 3-49 pg I-TEQ/l of fuel consumed. For each different oil the measured results varied, and there is clearly no simple, hard and fast relationship between chlorine in oil and emissions of dioxins from this engine. As can be seen from the figure there is no simple relationship between total chlorine input or chlorine contributed by the oil and the emissions.

Measurements of chloride and HCl in the exhaust consistently showed more chlorine in the exhaust than could be accounted for in the oil, fuel and air (typically 5 times as much).

If there is an effect of chlorine on the emissions it is not simple to discern from these data (see Figure 1). This is true when looking at the chlorine in oil, the total chlorine input or the measured chlorine in the exhaust.

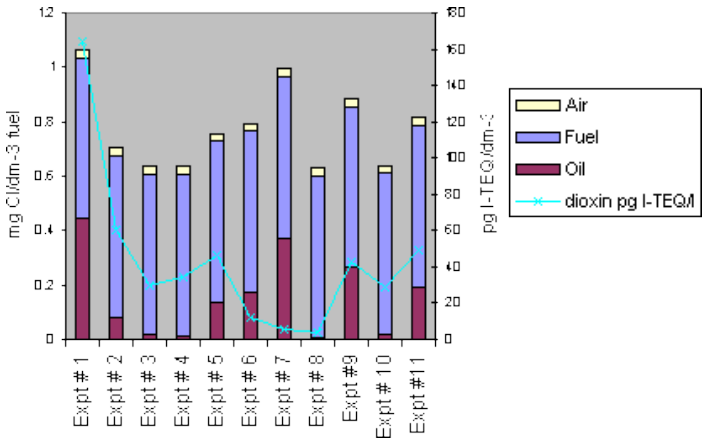

Figure 1 Contributions to chlorine load from air, fuel and oil and dioxin emissions

A potentially misleading relationship is suggested by the first run which resulted in the highest emissions by some margin. That test was considered flawed due to observed fouling of the probe from the conditioning run (the operational regime was subsequently changed to prevent this) but more significantly the results of the first tests appear to have been influenced by some unknown effect of the new engine at the outset of the testing. Emissions were consistently lower during later testing, note particularly run 7 using high oil, and it seems likely that either some contamination was present in the engine initially or there was some effect of conditioning the engine that affected the emissions.

PCB were also analysed in the samples collected (runs 1-8). In runs 3 to 8 no PCB were detected, in runs 1 and 2 PCB were detected at levels of 3.6 and 8.0 pg WHO TEQ/l which was low compared to the dioxins in those runs. As with the dioxin testing the PCB tests indicate that there may be some uncontrolled effect from insufficient engine conditioning that influenced the early test runs. Further data are required and improved detection limits will enhance the understanding of PCB emissions.

Conclusions

The testing measured not only dioxins in the emissions but also chlorine/chloride in the ambient air, the fuel and the oil and in the exhaust from the engine in order to assemble a chlorine balance. The testing could not account for all the chlorine found in the exhaust by summing the measured inputs.

The resulting data do not support the conclusion that the level of chlorine in the oil controls the emissions of dioxins from the engine. Furthermore, the data do not support the conclusion that the emissions of dioxins from the engine are controlled by the total chlorine present (either by summing the air, fuel and oil inputs or by looking at the measured chlorine in the exhaust).

There is no evidence from this testing (nor in the literature) that suggests that, in this range, the level of chlorine in the oil has a major effect on the emissions of dioxins from a vehicle.

Further testing is required, and is underway, to provide more comprehensive data on the effect of the oil and chlorine levels on emissions.

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References

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